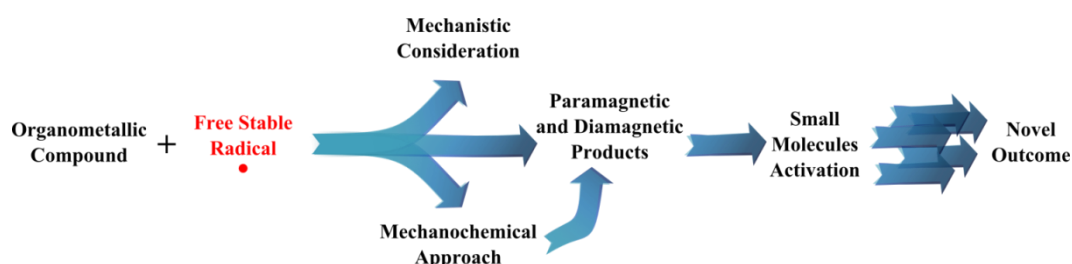


Our laboratory has been providing new looks at the old problems in chemistry for many years. For example, for over one and a half century the problem of controllable oxygenation of highly flammable organozinc compounds has been met with skepticism. However, our in-depth research revealed that in proper conditions this process leads to selected species. What is more, our further investigations extended our knowledge about this process to the point when it was possible to propose a new and plausible mechanism explaining the nature of the transformation.

Very recently we met a similar problem of reactions of free stable radicals (FSRs) with organometallics. These compounds are commonly utilized to scavenge alkyl radicals formed in organometallic reactions. What is, however, striking, whereas some authors affirmed that these species may react directly with substrates – organometallic species, others concluded that no such reaction occurs. These inconsistencies attracted our attention. Our initial investigations on the reactivity of the popular FSR – 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) towards diethylzinc ZnEt_2 were very encouraging. What is very interesting – the outcome of the reaction changes, depending on the sequence of addition of substrates. When TEMPO is added to diethylzinc $[\text{EtZn}(\text{TEMPO})]_2$ complex is formed, whereas addition of diethylzinc to TEMPO leads to $[\text{Zn}(\text{TEMPO})_2]_2$. Simultaneously with our publication, reactivity of $[\text{Zn}(\text{TEMPO})_2]_2$ towards dihydrogen H_2 was reported. Other reports clearly show that complexes supported by TEMPO become an emerging field in the activation of small molecules.



Mentioned facts became an impulse for more in-depth investigations on the reactivity of TEMPO towards organozinc species and organometallic compounds of group 13 (Al, In) to develop a general overview of these reactions. This task will be realized by examining model reactions of TEMPO with homoleptic R_nM (R = alkyl; M = Zn, Al, In) compounds as well as their complexes R_nML_x supported by multifunctional ligands L . This will hopefully allow for verification of the mechanism initially proposed for these reactions. Also, an integral task of this research will be probing the reactivity of TEMPO organometallic complexes obtained in previous step towards selected small molecules (H_2 , O_2).

Mechanochemistry considered as a way of breaking and forming new bonds by mechanical force, is experiencing its renaissance today. It is an established fact that during grinding of a material bonds break homolytically and radicals are formed. These radicals are responsible for stabilization of static charges of the material. It was recently demonstrated that doping polymers with small amounts of FSRs prevents static charging. However, doping materials with FSRs may have its limits. In our preliminary investigations we observed that that TEMPO may initiate the solid state reaction with organometallic species, but the outcome of this reaction is unknown. Probably the mechanism of this transformation is radical. What makes it truly interesting is the fact that, even though the knowledge on mechanochemistry advanced recently, no mechanochemical radical organometallic reactions were reported yet. In this project TEMPO will be utilized in mechanical force-induced reactions with organometallic compounds. In this regard, the mechanochemical part of this research can bring a new look at the chemistry of solid state transformations.